DEVELOPMENT OF PREDICTIVE REACTION MODELS
OF SOOT FORMATION

Annual Technical Report

Grant No. AFOSR 91-0129

Covering the period from January 1, 1991 to December 31, 1991

prepared for
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling AFB

by

Michael Frenklach

Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

January 31, 1991

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	January 31, 1992	Annual Technical 1/1/91 – 12/31/91

4. TITLE AND SUBTITLE
Development of Predictive Reaction Models of Soot Formation

6. AUTHOR(S)
Michael Frenklach

5. FUNDING NUMBERS
PE – 61102F
PR – 2308
TA – BS
G – 91 – 0129

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Pennsylvania State University
University Park, PA 16802

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NA
Building 410
Bolling AFB DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
This is a first-year annual report on the project. The ultimate objective of this program is to develop a predictive reaction model for soot formation in hydrocarbon flames. The specific objectives of the proposed 3-year study are to extend the modeling efforts to computer simulation and analysis of more complex sooting phenomena, such as sooting limits in laminar premixed flames, soot formation in premixed flames of aromatic fuels, and soot formation in laminar diffusion flames, and to further refine the underlying reaction mechanism of soot formation. During the first twelve-months period of the project, progress has been made in the following areas: development of a new optical model, simulation of sooting limits of laminar premixed flames; further development and testing of the detailed reaction mechanism for the formation and growth of polycyclic aromatic hydrocarbons (PAHs); and quantum-chemical potential energy calculations for ion-molecule reactions.

14. SUBJECT TERMS
Soot Formation, Computer Modeling

15. NUMBER OF PAGES
15

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

TABLE OF CONTENTS

INTRODUCTION

This is a first-year annual report on the project. The ultimate objective of this program is to develop a predictive reaction model for soot formation in hydrocarbon flames. The specific objectives of the proposed 3-year study are: 1) Following the successful accomplishments in soot formation model development under the previous grant (AFOSR 88–0072), which culminated in quantitative prediction of soot particle properties in several laminar premixed flames, the objective now is to extend the modeling efforts to computer simulation and analysis of more complex sooting phenomena, such as sooting limits in laminar premixed flames, soot formation in premixed flames of aromatic fuels, and soot formation in laminar diffusion flames, and 2) Further refinement of the underlying reaction mechanism of soot formation.

WORK PROPOSED

The specific objectives proposed are:

1. To compute several laminar premixed flames for different fuels and different stoichiometries in an attempt to simulate the sooting limits established experimentally by Glassman and co-workers, and having done that, to examine the factors determining the sooting limits in premixed flames.

2. To simulate soot particle formation in laminar premixed flames of benzene. This is important from both practical and fundamental points of view — many synthetic fuel have a high aromatic content, and the mechanism of soot formation from aromatic fuels is suggested to be somewhat different than from that of aliphatic hydrocarbons.

3. To initiate simulation of soot formation in laminar diffusion flame environments.

4. To undertake soot model reduction, i.e., to reduce the detailed reaction mechanism of soot formation to a small number of equivalent equations with the objective of economic coupling of soot formation chemistry with fluid-dynamic codes.

5. To reanalyze the PAH growth kinetics, in light of new finding that PAH condensation on soot particle surface is a significant mass-adding process.

6. To analyze theoretically the acetylene additions to aromatic radicals, which is one of the key reaction steps in PAH and soot particle growth. These reactions exhibit the highest sensitivities, yet their details and parameters have not been established. Of immediate concern is the energetics of acetylene addition to aromatic radicals and the dependence of the reaction rate coefficient on the aromatic-radical size.

7. To continue our collaborative studies with AeroChem on the role of ions in soot formation process.

RESULTS

During the first twelve-months period of the project, progress has been made in the following areas: development of a new optical model, simulation of sooting limits of laminar premixed flames; further development and testing of the detailed reaction mechanism for the formation and growth of polycyclic aromatic hydrocarbons (PAHs); and quantum-chemical potential energy calculations for ion-molecule reactions. The results obtained are detailed below.

New Algorithm for Powder Optical Properties

A computer algorithm was developed that calculates optical properties of an ensemble of particles whose size distribution is given in terms of moments of the size distribution function. This algorithm utilizes the lumping methods[1] and corresponding computational codes developed by us to model soot particle formation and growth in flames. It allows us to simulate light absorption and scattering without assuming a functional form for the particle size distribution, and thus to compare directly the numerical predictions of the model to the actual measured properties, such as intensity of scattered light determined by laser diagnostics. The new algorithm is being implemented and tested with the lumping code for soot particle formation.

Sooting Limits

Among principal experimental data available on soot formation in hydrocarbon combustion, critical equivalence ratios for soot appearance in laminar premixed flames,[2,3] ϕ_c, attract particular attention. Takahashi and Glassman[2] demonstrated that the values of ϕ_c for a wide range of fuels can be correlated by a remarkably simple relationship. It is of interest to see if this correlation can be predicted from first principles. Here we present the initial results of such efforts, using the recently developed reaction model for soot formation.[4]

The critical equivalence ratios in laminar premixed atmospheric $C_2H_6/O_2/N_2$ flames were calculated for three maximum flame temperatures (T_{max} = 1640, 1750 and 1855 K). For each of these temperatures a series of flame calculations was performed at different equivalence ratios. The maximum flame temperature in these calculations was kept constant by varying the amount of N_2 in the mixture. The calculations were performed in two stages. In the first stage, PAH formation up to coronene was simulated in a burner stabilized flame with a fixed temperature profile. This temperature profile was obtained from the equivalent free adiabatic flame calculated using small hydrocarbon chemistry (primarily C_1 to C_4). A description of the flame code used to carry out these calculations is given in Ref. 5. In the second stage, the computed profiles of H_2, H, C_2H_2, O_2, OH, H_2O and pyrene were used as input for the simulation of soot particle nucleation and growth, accomplished with an in-house kinetic code.[4] The gas phase and surface reaction mechanisms used in both stages of the calculations were those presented in Ref. 4.

Experimentally,[2,3] the critical equivalence ratio for the appearance of soot was determined by observing the onset of yellow light emission in a flame. In our simulations, the critical equivalence ratio ϕ_c was determined from the computed luminous intensity flux emitted by the soot particles. This luminous intensity flux, J, is given by

$$J = \int_0^x \int_{\lambda_{yellow}} j_\lambda \, d\lambda \, dx \ , \tag{1}$$

where x is the height above the burner, λ the wavelength, j_λ the monochromatic radiant density flux for a radiation medium of a unit volume containing n particles of size d. Based on Kirchhoff's law,[6] we have

$$j_\lambda = \alpha_\lambda B_\lambda(T) \ . \tag{2}$$

The Planck function for an isotropic emitter, $B_\lambda(T)$, and the absorption coefficient, α_λ, in Eq. (2) are defined as

$$B_\lambda(T) = \frac{2hc^2/\lambda^5}{e^{hc/\lambda kT} - 1} \ , \tag{3}$$

and

$$\alpha_\lambda = n \, \frac{\pi d^2}{4} \, Q_{abs} \ , \tag{4}$$

respectively, where h is Planck's constant, c the speed of light, λ the wavelength, k Boltzmann's constant, T the temperature, and Q_{abs} the absorption efficiency. The monochromatic radiant density flux j_λ for a system of particles of non-uniform particle sizes is given by

$$
\begin{aligned}
j_\lambda &= \sum_{i=1}^{\infty} \alpha_{\lambda,i} \, B_\lambda(T) \\
&= B_\lambda(T) \sum_{i=1}^{\infty} n_i \, \frac{\pi d_i^2}{4} \, Q_{abs,i} \ ,
\end{aligned}
\tag{5}
$$

where the subscript i denotes a particle of size i and n_i and d_i are the number density and the diameter of particles of size i, respectively. The Mie absorption efficiency, $Q_{abs,i}$, is calculated from

$$Q_{abs,i} = Q_{ext,i} - Q_{sca,i} \ , \tag{6}$$

where both the extinction efficiency, $Q_{ext,i}$, and the scattering efficiency, $Q_{sca,i}$, are expressed as functions of particle size and wavelength using the formulas of Penndorf.[7] The complex refractive index in our calculations was taken from Chang and Charalampopoulos.[8] The summation in Eq. (5) was evaluated from the moments of the particle size distribution. These moments were calculated using the method of Frenklach and Harris.[9]

6

Figure 1 shows the computed luminous intensity flux as a function of the equivalence ratio at several heights above the burner for flames with maximum temperature of 1640 K. The same fluxes, but now each curve, at a given height, scaled to its maximum value, are plotted in Fig. 2. These scaled curves were used to determine the critical equivalence ratio corresponding to the maximum flame temperature. We assumed that the critical equivalence ratio is reached when the luminous flux undergoes a sudden rise illustrated in Fig. 2.
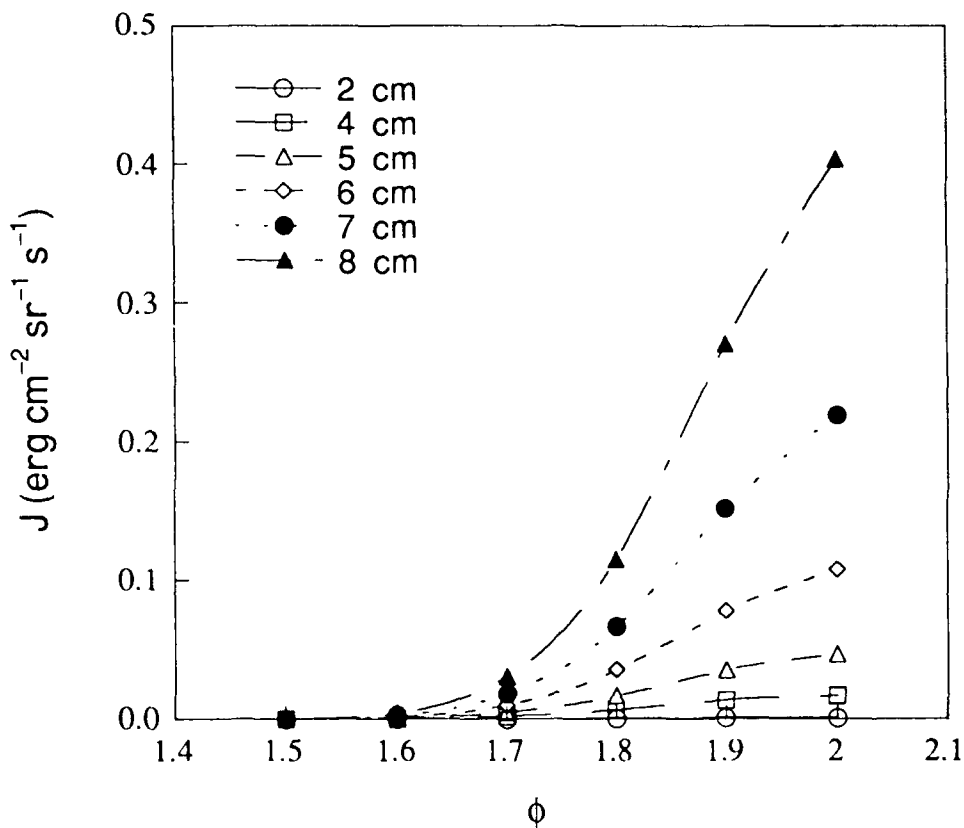

Figure 1. Computed luminous intensity flux for the $C_2H_6/O_2/N_2$ flames with T_{max} = 1640 K.

The critical equivalence ratios determined in this manner are compared with the experimental data of Harris et al.[3] in Fig. 3. As can be seen in this figure, a reasonable agreement is achieved. In this study, we also examined the effect of the maximum flame temperature on the flame sooting tendency. The results for an equivalence ratio of 1.7 are shown in Fig. 4. The bell-shaped dependence of the luminous intensity flux on temperature shown in this figure, is in accord with that observed for the soot volume fraction in the experiments of Böhm et al.[10] for acetylene-, ethylene- and benzene-air flames.
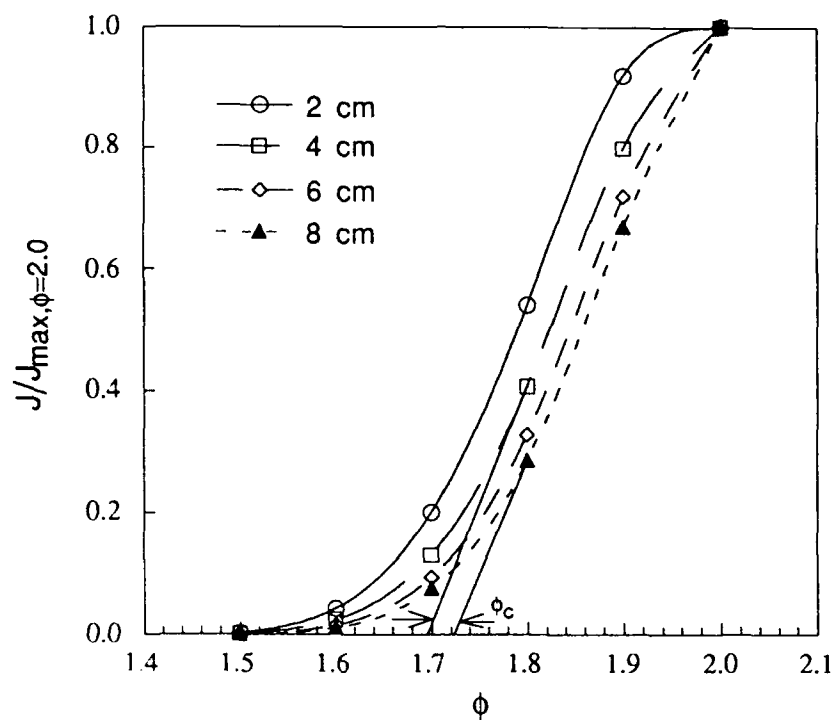
7

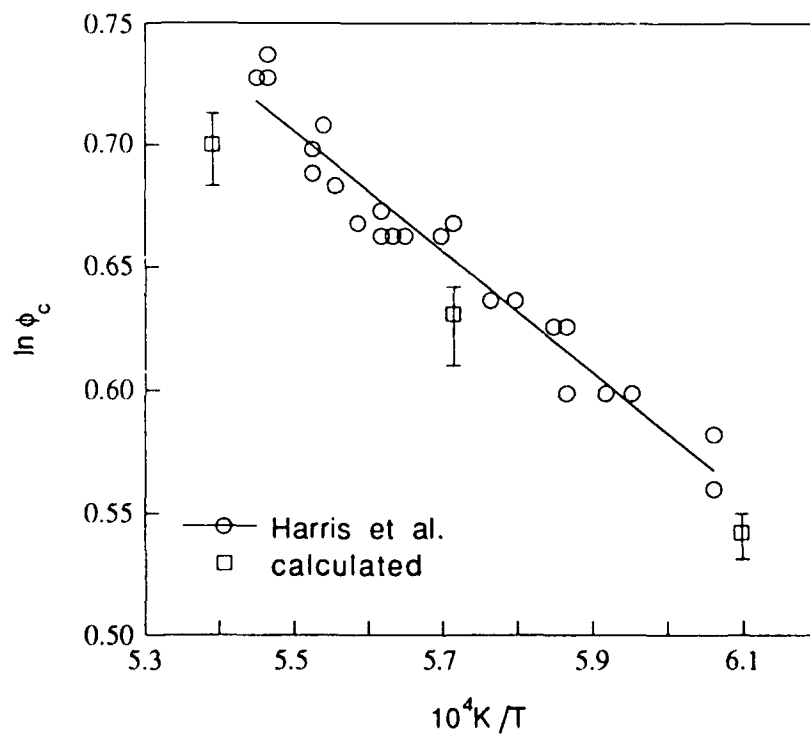Figure 2. Relative luminous intensity flux for the $C_2H_6/O_2/N_2$ flames with T_{max} = 1640 K.

Figure 3. Comparison of the computed and experimentally determined[3] critical equivalence ratios of $C_2H_6/O_2/N_2$ flames.
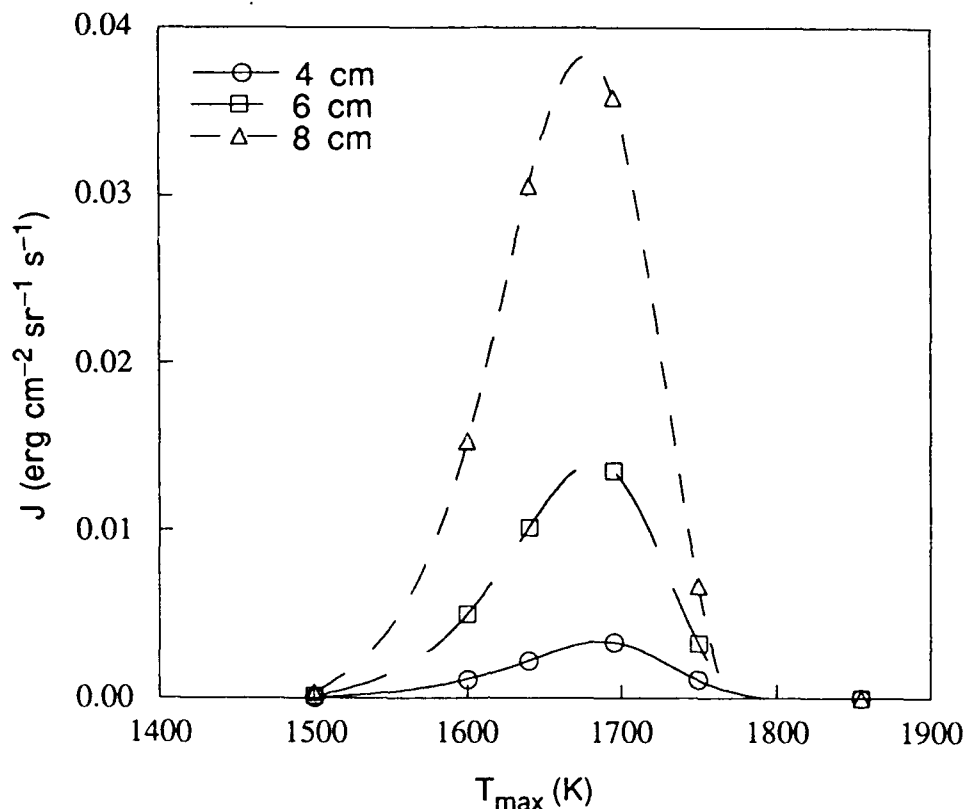
Figure 4. Computed luminous intensity flux as a function of maximum flame temperature for the $C_2H_6/O_2/N_2$ flames with $\phi=1.7$.

Neutral Reaction Mechanism

In a recent review article on chemical kinetics and combustion modeling, Miller, Kee and Westbrook[11] suggested that the above cyclization reactions cannot be responsible for the formation of the first aromatic ring because the concentrations of n–C_4H_3 and n–C_4H_5 radicals should be low since the reactions

$$H + n\text{–}C_4H_3 \rightleftharpoons H + i\text{–}C_4H_3 \tag{7}$$

$$H + n\text{–}C_4H_5 \rightleftharpoons H + i\text{–}C_4H_5 \tag{8}$$
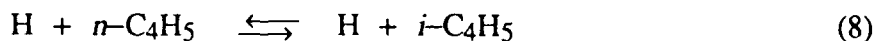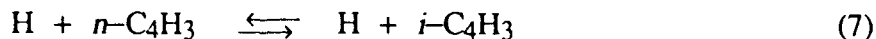
deplete the concentrations of the n–isomers required for the cyclizations. Reactions (7) and (8) were not included in our model initially, because the computational results indicated that the n– and i–isomers are already equilibrated by several other reactions in the system. Nonetheless, to test the Miller et al.'s suggestion, we performed additional simulations of the three laminar premixed flames we analyzed previously.[4,12] The reactions (7) and (8) were now included in the simulations assuming rate coefficients 1×10^{14} mol cm^{-3} s^{-1} for the exothermic directions. The results of these simulations for all the three flames tested in Refs. 12 indicated that the inclusion of reactions (7) and (8) — even with upper-limit rate coefficient values — does not make a difference on the computed profile of benzene.

As an alternative, Miller et al.[11] suggested that benzene is formed by combination of propargyl radicals producing benzene or phenyl. A similar proposal was made by Alkemade and Homann[12] and Stein et al.[14] Figures 5 and 6 show the results of flame simulations with reaction

$$C_3H_3 + C_3H_3 \rightleftharpoons \text{(benzene)} \qquad (9)$$
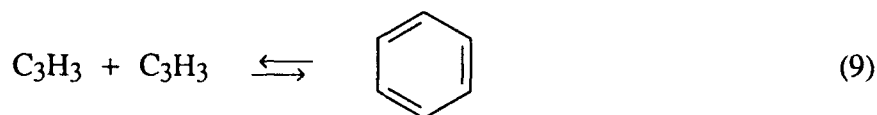
included with the rate coefficient of $5 \times 10^{12} \, \text{mol} \, \text{cm}^{-3} \, \text{s}^{-1}$ suggested by Stein et al.[14] Analysis of these results indicate that the inclusion of cyclization channel (9) does not *always* increase the production rate of benzene, as clearly shown in Fig. 5 for the flame conditions of Harris and co-workers.[15] For the conditions of the Westmoreland's flame,[16] the inclusion of reaction (9) significantly overpredicts the amount of benzene determined experimentally (Fig. 6). This is clearly a challenging issue, as the reaction chemistry of C_3H_x species is not well known.
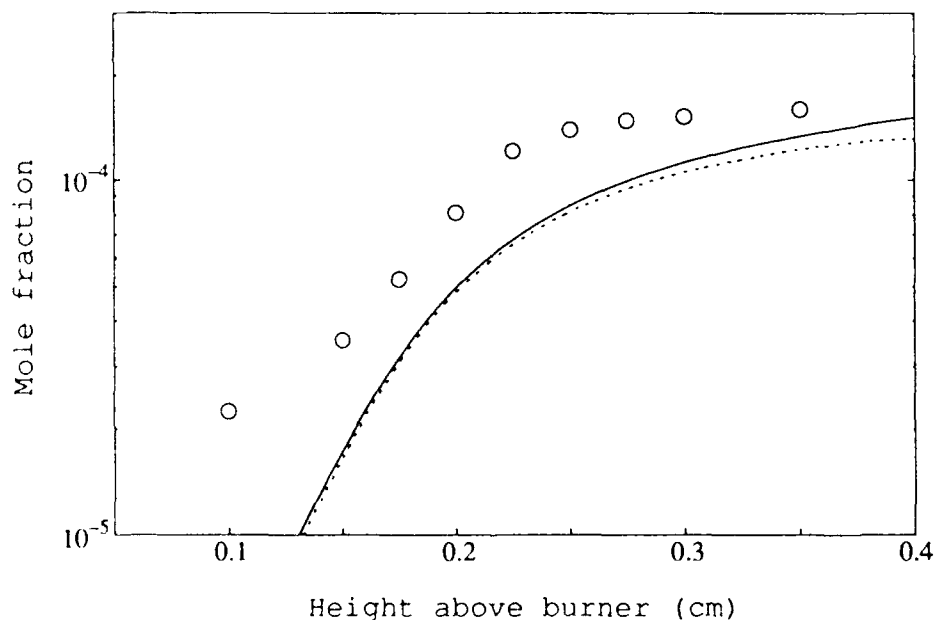

Figure 5. Benzene mole fraction: circles — experimental data,[15] solid line — computed with the mechanism used in Refs. 4 and 12, dotted line — computed with reaction (9) included
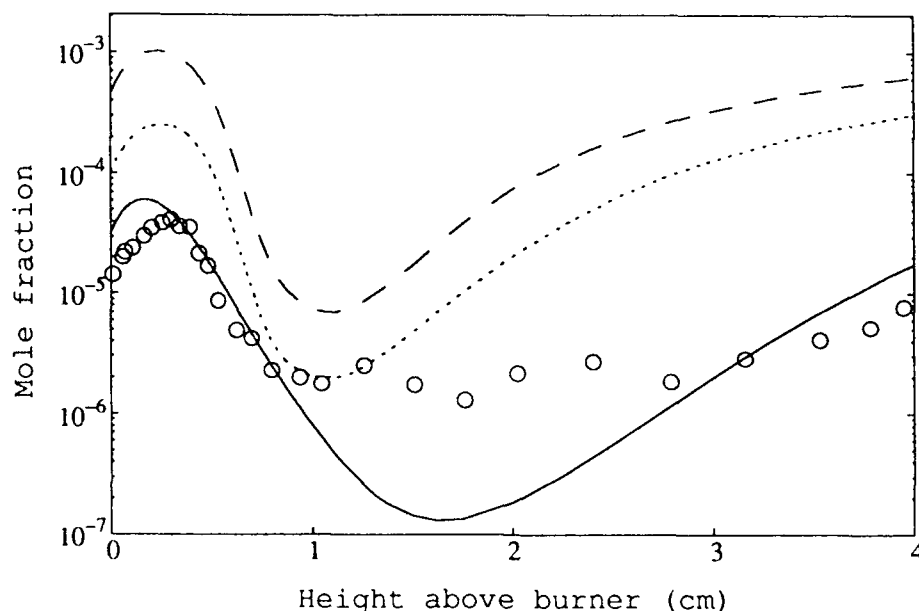
Figure 6. Benzene mole fraction: circles — experimental data;[16] solid line — computed with the mechanism used in Refs. 4 and 12; dashed and dotted lines — computed with reaction (9) included, dotted line represents the result computed with the mechanism tuned to fit the experimental C_3H_3 profile

Ionic Reaction Mechanism

To evaluate the rate coefficients for some of the key ion-molecule reactions in the AeroChem reaction mechanism[17] suggested for the ionic pathway to soot, potential energy calculations were performed for reaction

$$C_8H_7^+ + C_2H_2 \rightarrow C_{10}H_9^+ .$$
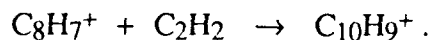
The calculations were performed on various ions using the MOPAC semi-empirical quantum chemical program. For each proposed structure a geometry optimization was performed using the AM1 hamiltonian utilizing a BFGS update technique. A force analysis of the stable geometries, again using MOPAC, confirmed that these were indeed local minima in the AM1 potential energy surface. The force analysis was carried out at 298 K and in the ground state rotational level. In order to find transition states between these structures the SADDLE facility of MOPAC was used that interpolates between given reactant coordinates and product coordinates. Several transition states found in this manner were confirmed to be so by a force analysis showing one imaginary root of the force matrix. The potential energy diagram is shown in Fig. 7. Calculations of the rate coefficients based on these data are in progress.
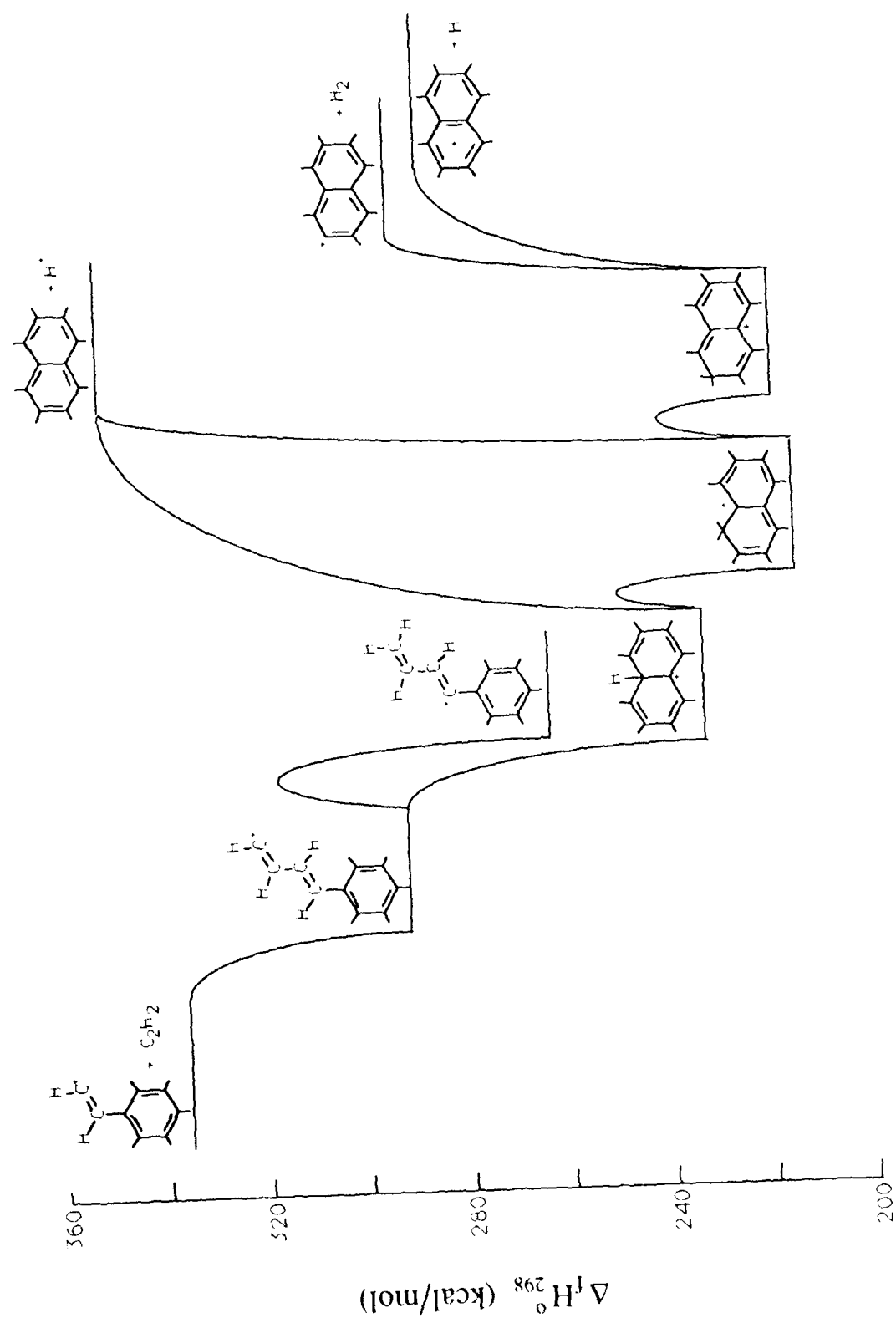
11

Figure 7. Potential enrgy diagram for reaction $C_8H_7^+ + C_2H_2 \rightarrow C_{10}H_9^+$

FUTURE WORK

The objectives for the next year are the following:

1. To complete simulations of the sooting limits and examine the results.

2. To complete the revision and testing of the neutral reaction mechanism of PAH formation and growth. The work is currently in progress on re-evaluation of thermodynamic and kinetic data for key PAH species and reactions.

3. To revise the computer code for soot particle nucleation and growth. The optical model developed, after being successfully tested, is being "inserted" into our main code.

4. To perform quantum-chemical calculations on additional ion-molecule reactions of interest to the ionic mechanism of soot formation and preform the associated rate-coefficient calculations.

5. To initiate a computational study of pressure effect on soot formation. This subject is of interest due to growing concern over controlling soot emission from diesel engines.

6. To prepare manuscripts reporting the results of (1) – (4) above.

PRESENTATIONS AND PUBLICATIONS

1. Frenklach, M., "Mechanism and Modeling of Soot Formation," Princeton University, Department of Mechanical and Aerospace Engineering, February 19, 1991.

2. Frenklach, M., "Mechanism and Modeling of Soot Formation," NASA-Lewis Research Center, Cleveland, OH, March 25, 1991.

3. Frenklach, M., "What are the Barriers to Modeling Soot Formation and Oxidation in Diesels and Gas Turbines?" ARO Conference on *Particulates in Heterogeneous Combustors*, Boulder, CO, June 12–13, 1991 (a keynote lecture).

4. Frenklach, M. and Wang, H., "Aromatics Growth beyond the First Ring and the Nucleation of Soot Particles, *Preprints of the 202nd ACS National Meeting*, Vol. 36, No. 4, 1991, p. 1509.

5. Frenklach, M. and Wang, H., "Detailed Mechanism and Modeling of Soot Particle Formation," International Workshop on *Mechanisms and Models of Soot Formation*, Heidelberg, September 29–October 2, 1991.

6. Frenklach, M., "Chemistry and Modeling of Soot Formation," University of Wisconsin, Madison, Department of Mechanical Engineering, November 12, 1991, (Hall Lecture seminar series).

7. Markatou, P., Wang, H., and Frenklach, M., "A Computational Study of Sooting Limits in Laminar Premixed Ethane/Oxygen/Nitrogen Flames," Twenty-Fourth Fall Technical Meeting of the Eastern Section of the Combustion Institute, 1991, Paper 10.

8. Frenklach, M. and Wang, H., "Detailed Modeling of Soot Particle Nucleation and Growth," *Twenty-Third Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1991, p. 1559.

9. Frenklach, M., "Reduction of Chemical Reaction Models." in *Numerical Approaches to Combustion Modeling* (E. S. Oran and J. P. Boris, Eds.), Progress in Astronautics and Aeronautics, Vol. 135, American Institute of Aeronautics and Astronautics, Washington, D.C., 1991, p. 129.

10. Frenklach, M., "Development of Chemical Reaction Models," in *Chemical Reactions in Complex Systems* (A. V. Sapre and F. J. Krambeck, Eds.), Van Nostrand Reinhold, 1991, p. 197.

PROFESSIONAL PERSONNEL

Dr. Michael Frenklach — Principal Investigator

Dr. Brian Weiner — Participating Faculty

Dr. Penelope Markatou — Postdoctoral Scholar

Mr. Hai Wang — Graduate Student

INVENTIONS

None.

REFERENCES

1. Frenklach, M., in *Complex Chemical Reaction Systems, Mathematical Modelling and Simulation* (J. Warnatz and W. Jäger, Eds.), Springer-Verlag, Berlin, 1987, p. 2; in *Numerical Approaches to Combustion Modeling* (E. S. Oran and J. P. Boris, Eds.), Progress in Astronautics and Aeronautics, Vol. 135, American Institute of Aeronautics and Astronautics, Washington, D.C., 1991, p. 129.

2. Takahashi, F. and Glassman, I., *Combust. Sci. Technol.* 37, 1 (1984).

3. Harris, M. M., King, G. B. and Laurendeau, N. M., *Combust. Flame* 64, 99 (1986); 67, 269 (1987).

4. Frenklach, M. and Wang. H., *Twenty-Third Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1991, p. 1559.

5. Kee, R. J., Grcar, J. F., Smooke, M. D., and Miller, J. A., Sandia Report No. SAND85-8240, 1985.

6. Rybicki, G. B. and Lightman, A. P., *Radiative Processes in Astrophysics*, Wiley, New York, 1979, Chapter 1.

7. Penndorf, R. F., *J. Opt. Soc. Amer.* 52, 896 (1962).

8. Chang, H. and Charalampopoulos, T. T., *Proc. Roy. Soc. Lond. A* 430, 577 (1990).

9. Frenklach, M. and Harris, S. J., *J. Colloid Interface Sci.* 118, 252 (1987).

10. Böhm, H., Hesse, D., Jander, H., Lüers, B., Pietscher, J., Wagner, H. Gg. and Weiss, M. *Twenty-Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1989, p. 403.

11. Miller, J. A., Kee, R. J. and Westbrook, C. K., *Annu. Rev. Phys. Chem.* 41, 345 (1990).

12. Wang, H. and Frenklach, M., "Modeling of PAH Profiles in Premixed Flames," Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Albany, New York, October 1989.

13. Alkemade, U. and Homann, K. H., *Z. Phys. Chem. N. F.* 161, 19 (1989).

14. Stein, S. E., Walker, J. A., Suryan, M. M., and Fahr, A., *Twenty-Third Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1991, p. 85.

15. Harris, S. J., Weiner, A. M., Blint, R. J., and Goldsmith, J. E. M., *Twenty-First Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1988, p.1033; Harris, S.J., Weiner, A.M., and Blint, R.J., *Combust. Flame* 72, 91 (1988).

16. Westmoreland, P. R., "Experimental and Theoretical Analysis of the Oxidation and Growth Chemistry in a Fuel-Rich Acetylene Flame," Ph.D. thesis, MIT, 1986.

17. Calcote, H. F. and Gill, R. J., *Computer modeling of soot formation comparing free radical and ionic mechanisms*, Final Report to AFOSR, TP–495, 1991.